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Transmission of a Drift Tube Ion Mobility Spectrometer, Connected with a Mass Spectrometer

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Abstract

In this work it is experimentally showed that transmission of atmospheric drift tube ion mobility spectrometer (DT-IMS), connected with mass spectrometer (MS), depends on ion mobility of investigated compounds, because of depletion effect of Bradbury-Nielson ion gate (IG), which previously has been approved only by standalone DT-IMS. Theoretical estimation of depletion width of IG is in good agreement with experimental data. Also it is found, that ion lost due to its pulsing work of IG are few times smaller, than its duty cycle. It's explained by difference in influence of coulomb repulsion at 100% and 1% duty cycle – in first case it's significant versus second case, when coulomb repulsion become negligibly small, that reduces lost of ions on entrance of MS interface.

Keywords: IMS/MS, drift ion mobility spectrometry, time-of-flight mass spectrometry, bradbury-nielson ion gate, transmission

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1. Introduction

Atmospheric drift tube IMS is convenient independent add-on equipment for existing MS, which allow one to upgrade it and, consequently, expand measured ratio of mass to charge distribution with additional dimension – ion mobility, without necessity to change one of the most expensive lab instrument - MS. For reaching this goal one need to install ion mobility part between atmospheric ion source and MS interface, and synchronize electronics of IMS and MS to be able to work with IMS/MS spectra in standard MS software as with LC/MS spectra, keeping in mind about 1,000 speed up in time of IMS separation, comparing with LC [1–3]. But significant disadvantage of such connection is its very high ion lost more than 99,99% [4], which motivates development of much more serious hybrid MS with reduced pressure DT-IMS built into an interface [5,6]. In case of low duty cycle different approach exist, which allows one to increase ion efficiency particularly to 50% [7,8]. In the case of ion loss, happens during crossing from IMS to MS interface (which usually made as small orifice less than 1 mm diameter), there is no effective ion focusing technology between atmospheric region and rough vacuum of 1st stage MS interface. Due to radial broadening of ion flow in DT-IMS [9]), and very small diameter of orifice – transmission of ion current into interface is smaller than 1%.

The purpose of this work is experimental investigation of ion transmission efficiency using IMS/TOF MS prototype [10]: whole transmission, depletion effect of IG, which previously had been tested only on standalone IMS [11,12], and check influence of coulombic repulsion at ion transmission, which previously had been reviewed from the resolution point of view [13].

2. Experimental

Custom made IMS/TOFMS [10] has two working regime of IG – fast & open. In first case IG opens for short period of time τ_g = 0,5 ms, comparing to period of IMS T_{IMS} = 51,2 ms (or duration of whole mobility spectrum). Consequently, duty cycle ($\eta_{fast} = \tau_g / T_{IMS}$) has very small value less than 1%. On the other hand, in second regime "open IG" – IG keeps open all the time ($\tau_g = T_{IMS}$) and η_{open} = 100%. First order estimation tells us that ratio of ion intensities in these two regimes must be about ratio of its duty cycle, i.e. $\eta_{fast} / \eta_{open} \sim 1\%$. But experimental results gives few times bigger value circa 1,5 - 2,2%.

Testing sample was made of 6 compounds in broad range of ion mobilities (0.8-1.5 cm^2/V·s): 12 uM lomefloxacin (Lom) and ofloxacin (Ofl), 2 uM tetraalkylammonium halides (TAAH3, -5 and -8), 0.5 uM 2,6-di-tert-butylpyridine (2,6-DtBP), - dissolved in MeOH with 1% Acetic Acid. Ratio of mass spectra ion intensities (square of ion peaks), got in fast and open regime (S_{fast} / S_{open}), defines interested efficiency of working IMS ($\eta_{fast} / \eta_{open}$), connected with MS (see Table 1).

Table 1. Experimental data

Initial compound	**2,6-DtBP**	**TAAH3**	**TAAH5**	**Lom**	**Ofl**	**TAAH8**
K_0, **cm^2/V·s**	1.48	1.46	1.11	1.08	1.05	0.80
m/z	192.17	186.22	298.35	352.14	362.15	466.54
$\eta_{fast} / \eta_{open} = S_{fast} / S_{open}$	2.2%	2.3%	1.9%	1.9%	1.7%	1.5%

It's clear from table that reduced ion mobility correlates with IMS efficiency: $K_0 \sim \eta_{fast} / \eta_{open}$. This dependence caused by IG depletion effect [11,12], which based on two simple facts: IG has finite length in drift direction l_{depl} and ion drift velocity V_{ion} relatively slow. Consequently, ion time of flight of IG region $tof_{IG} = l_{depl} / V_{ion}$ comparable to IG open time τ_g, i.e. $tof_{IG} \sim \tau_g$. That's why all ions, that have not passed IG (its length l_{depl}) during its open time τ_g, destroying very fast after IG closing.

Another important observation is exceeding experimentally obtained IMS efficiency $\eta_{fast} / \eta_{open}$ over its theoretical first order estimation. We suggesting that it's caused by coulombic repulsion. Or, more precisely, by its different influence on radial broadening in open and fast IMS regime, that is the consequence of variety in ion density and form of flow. Indeed, uninterrupted ion flow produced in open regime and tiny ion bunches in fast one differing not only by a few orders of magnitude of ion current, but also by number of degree of freedom (three and two, respectively).

3. Theoretical estimations

To check our suggestions we've built two models. First is the IG drift region simulation, made in Simion 8, allowed to value IG depletion length l_{depl}. Second is the estimation of coulombic repulsion influence in open and fast regime. And the last, third, is IMS efficiency (η_{fast} / η_{open}) in form of analytical expression. This model, with estimations from other, allowed comparing experimental and theoretical data of IMS efficiency in IMS/MS instrument. Let's look at these models closer.

The first model is the profile of electrical potential distribution around closed IG shown in Fig. 1. And black hatched region near wires is the part of volume, in which direction of electrical field is opposite to drift movement, which equal to X axis. Summary length of these regions in X axis direction, i.e. length of depletion zone, is l_{depl} = 0.6 mm and very close to distance between wires (in radial direction), as expected by rough estimation.

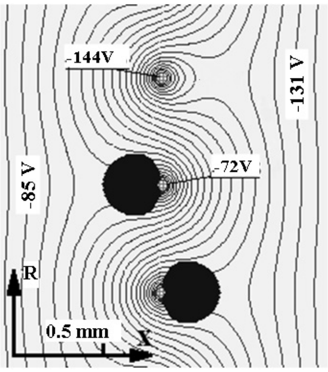

Fig. 1 Electrical potential distribution of closed IG

The second model is the radial broadening of initial ion flow (***I*** = 10^{-8} A) through ion source – IMS entrance hole (***D*** = 6 mm) in approximation of "infinite" cylinder and "spherical" ion clouds at open and fast IMS regime, respectively. As it known from Gauss-Ostrogradsky's theorem, electrical field is inversely proportional to linear and square power of radius in these approximation, respectively too. Solution of simple differential equation $V_{ion} = \mathrm{d}r/\mathrm{d}t = E(r)\cdot K$ increase its power to square and cubic. In result, radius of ion flow in IG cross-section is 18 mm, that is starting condition for comparing both regimes. In open regime, at the end of IMS, before entering into interface of MS through tiny orifice (radius 0.15-0.2 mm), radius of ion flow achieving 29 mm. But in case of working, fast regime with small time of open IG (τ_g = 0,5 ms), its coulombic repulsion is negligible, i.e. 18 mm retains. Because ion density defines by squared radius, then IMS efficiency due to influence of coulombic repulsion increase in β = 2.6 times.

$$\frac{\eta_{fast}}{\eta_{open}} = \frac{\tau_g}{T_{\mathrm{IMS}}}\left(1-\frac{l_{depl}}{\tau_g V_{ion}}\right)\beta = A - B\frac{1}{K_0}$$

The last model is the analytical expression on base of IG duty cycle (τ_g/T_{IMS}), depletion effects (inside parenthesis) and correction coefficient (β), characterizing coulombic repulsion influence, where A and B are coefficients for experimental data interpolation. Hence, we can experimentally define two parameters, i.e. l_{depl} and β. Theoretical estimation gives 1.1-1.7% of IMS efficiency.

4. Results and discussion

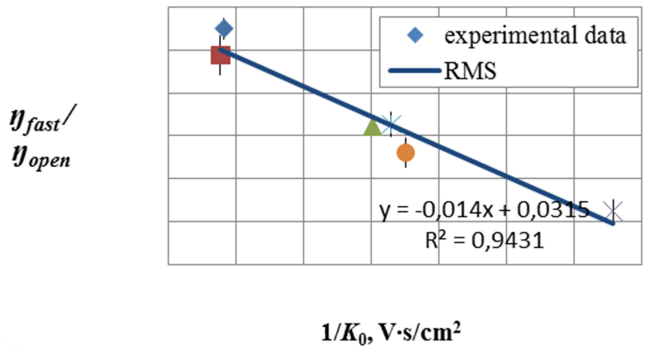

Fig. 2 Experimental data and root mean square interpolation of IMS efficiency in dependence of reduced ion mobility.

Experimental data with interpolation by theoretical model by root mean square (RMS) method shown on Fig. 2. Linear theoretical model satisfactory correlate with experimental data. On base of interpolation coefficient ***A*** and ***B*** estimated: l_{depl} = (0.75 ± 0.1) mm, 12% and β = (3.6 ± 0.2), 5%. Depletion length is in good agreement of theoretical evaluation. In case of coulombic repulsion coefficient β, difference 5 times bigger, than its uncertainty, that can be attributed to first order approximations and influence on ion movement in MS interface.

5. Conclusion

Efficiency of IMS, connected with MS, estimated theoretically and valued 1.1-1.7%. Duty cycle of Bradbury-Nielson ion gate, its depletion effect and variety in influence of coulombic repulsion on ion density before entrance into MS interface in pulsing (fast) and open regime of IG work were taken into account. Experimental measurement demonstrated satisfactory agreement of 1.5-2.2%. Difference can be associated with first order approximations and influence on ion movement in MS interface.

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